

EMULSION POLYMERIZATION OF BUTYL ACRYLATE: SPIN TRAPPING AND EPR STUDY

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SYNOPSIS

The propagating radical in the emulsion polymerization reaction of butyl acrylate was detected by Electron Paramagnetic Resonance (EPR) spectroscopy using two spin trapping agents, 2-methyl-2, 2-nitrosopropane (MN⁺) and α -(4-pyridyl)-N-tert-butyl nitron (PyOBN). Through analysis of hyperfine structure of the spectra obtained from the trapped radicals, the propagating radical is inferred to be the well known acrylate radical, $-\text{[CH}_2-\text{CH}(\text{COOC}_4\text{H}_9)]_n-\dot{\text{C}}\text{H}(\text{COOC}_4\text{H}_9)-$.

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INTRODUCTION

Since its development during World War I, the emulsion polymerization process* has become popular as a convenient method for the production of acrylic polymers. The process is commonly carried out in an emulsion of two phases, an aqueous phase and a non-aqueous phase. Compared to bulk processes, the emulsion polymerization process has advantages such as safety of the aqueous reaction medium, faster rate of polymerization with good control, production of polymers with higher molecular weight (by a factor of 10) as well as different molecular weight distributions, and excellent yield of final product in a form suitable for many applications. There are two commonly used initiation techniques for emulsion polymerization; ^{1,2} "reflux method," in which the initiating radicals are produced by a thermally sensitive initiator such as a peroxide or azo compound through external heating and subsequent refluxing of monomers, and "redox method," in which a peroxide or other oxidizing initiator is used in combination with a reducing agent (a redox couple), usually without the need for any external heating. In this work, the redox method was used for initiation of free radical emulsion polymerization.

As a first step toward mechanistic understanding of a free radical polymerization, it is important to characterize the propagating radical specie(s) involved in the process. Direct observation by EPR spectroscopy of propagating free radicals in emulsion polymerization has been reported in the case of methyl methacrylate (MMA), either by a quick freeze method^{3,6} or by in-situ flow cell observations.^{7,8} Initially we made an attempt to observe the propagating radical for the emulsion polymerization of n-butyl acrylate (BA) with a quick freeze method (to 77°K, on the time scale of ~3 sec.). However, it appears that under reaction conditions normally used for polymerization, the lifetime of BA propagating radical is too short to allow quenching by freezing before essentially complete termination has occurred, or else the instantaneous radical concentration is extremely low. We estimate that the detection limit for poly(n-butyl acrylate) (PBA) propagating radicals in the freezing experiment was roughly 10^{-7} M. Rough estimation of the concentration of PBA propagating radicals based on the relative values of the propagation rate constant for BA and MMA, and the concentration of poly(methyl methacrylate) (PMMA) propagating radicals observed

in emulsion polymerization, is consistent with the concentration of the PBA propagating radicals being near or below our detection limit. As an alternative approach, a spin-trapping technique was employed for observing the propagating radicals.

In the spin trapping technique,^{9,10} short-lived radicals are reacted with appropriate trapping agents and converted to relatively stable nitroxide radicals (spin adducts). The structure of the trapped radical can be deduced from the analysis of EPR spectrum of the spin adduct, and at least some structural information is usually obtained. There are two types of trapping agents which are most frequently used: nitroso and nitron compounds. Such spin trapping agents have been reported in the literature for characterization of propagating radicals in radical polymerization reactions, such as in polymerization of styrene, vinyl monomers¹¹⁻¹³ such as methyl acrylate, ethyl acrylate and MMA, and dialkyl fumarates.¹⁴ In this work two spin traps, 2-methyl-2-nitrosopropane (MNP) and α -(4-pyridyl 1-oxide)-N-tert-butyl nitron (PyOBN), were used for the detection of propagating radicals in the emulsion polymerization of BA.

EXPERIMENTAL

Chemicals Spin traps used in the experiments, MNP(dimer), PyOBN, and other chemicals such as detergents, Triton X-100, sodium dodecyl sulfate, and redox initiators, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and sodium bisulfite (NaHSO_3), were purchased from Aldrich Chemical Co. BA and methacrylic acid were obtained from Rohm and Haas Co. All chemicals were used as received.

Emulsion Polymerization Procedure for the emulsion polymerization (batch operation) was adapted from a publication of Rohm and Haas,² "Emulsion Polymerization of Acrylic Monomers," and also from Spada et al.⁵ (Column 17, example 1): The monomer premixture was prepared by mixing butyl acrylate (98.5 wt%) and methacrylic acid (1.5 wt%). Deionized water and the monomer premixture were deoxygenated by bubbling N_2 gas overnight before use. In a round bottom flask (1000 ml), deionized water (80 ml), surfactants, non-ionic detergent (Triton X-100, 5 g) and ionic detergent (sodium dodecyl

sulfate, 0.35 g), and small amount of monomer premixture (10 ml) were added with mechanical stirring. During the polymerization, the reaction flask was maintained under N_2 atmosphere through bubbling. After stirring for 30 min., monomer premixture (130 ml) was added dropwise over a 30 min. period. Aqueous solutions of initiators, $Na_2S_2O_8$ (1.4 g/15 ml) and $NaHSO_3$ (0.6 g/5 ml), were added one after the other over a 10 min. period.

The spin trap solutions were prepared in deoxygenated water prior to use. In the case of MNP, the dimer was dissolved in pre-deoxygenated water (0.25 g/50 ml) in an Erlenmeyer flask (12.5 ml). The flask was briefly flushed with N_2 gas and stoppered. The solution was stirred overnight by a magnetic stirrer at room temperature in the dark to achieve MNP monomer-dimer equilibrium. The other spin trap, PyOBN, was dissolved in deoxygenated water (~0.4 g/25 ml) just before use.

About 15-30 min. after the addition of catalyst solutions, the reaction temperature started to rise, and finally to 60~90°C. For the spin trapping experiments, the aqueous solution of spin trapping agent was added to the reaction flask when the temperature rose to ~45°C. The final concentrations of the spin traps used for trapping propagating radicals in the emulsion polymerization were 0.005 M for MNP and 0.008 M for PyOBN. After the addition of spin traps, the temperature started to decrease and reached room temperature in ~30 min. The first sample was taken 5 min. after addition of the spin trap, and additional samples were taken in 3-5 min. intervals to a total of 10 samples. This was done to detect possible changes in the degree of polymerization of the spin adducts as can be reflected in the hyperfine coupling constants or the mobility of the spin adducts.

For trapping initiating radicals, the initiator solutions, $Na_2S_2O_8$ and $NaHSO_3$, were added to the spin trap solution one after the other with shaking.

EPR Experiments A commercial EPR spectrometer (Bruker ESP 300) operating at X-band frequency (9.5 GHz) and employing 100 kHz field modulation was used. The spectrometer is equipped with a digital spectral manipulation capability.

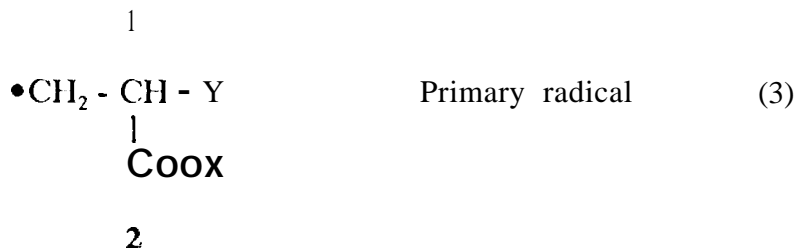
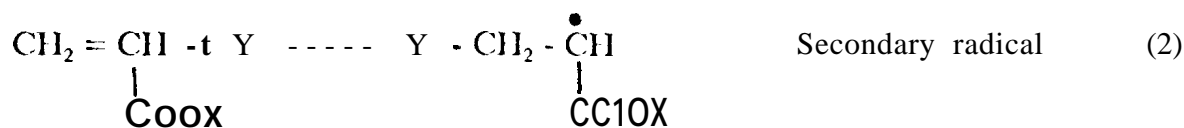
The emulsion was sampled in pyrex capillary tubings (0.75 mm ID x 1.0 mm OD x 100 mm Length, Glass Company of America, Bargain town, NJ.) to a height of -2 cm, and bottom ends were sealed with vacuum grease (Apiezon N). Samples of 7 capillaries (total sample volume of 65 μ l) were then placed in a standard fused silica EPR sample tube (4 mm OD x 3 mm ID x 250 mm Long, Wilmad Glass Co., Buena, NJ.) and analyzed in the microwave cavity (TE₁₀₂ mode) at room temperature. Each spectrum was obtained with a microwave power of 4.9 mW, field modulation amplitude of 0.1 -0.5 Gauss. A microwave frequency counter (HP 5342A) and a proton NMR gaussmeter were used.

RESULTS AND DISCUSSION

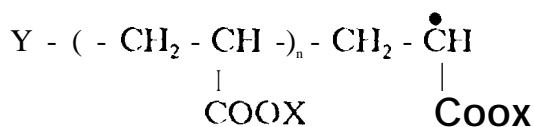
In the aqueous redox polymerization reactions¹⁶ with persulfate initiator (Na₂S₂O₈) and an activator (NaHSO₃), the initiation reaction produces radical ions such as sulfate, $\bullet\text{SO}_4^-$, and sulfonate, $\bullet\text{SO}_3^-$. Depending on the pH of the solution, the sulfate radical can further react with water to produce hydroxyl radicals, $\bullet\text{OH}$.



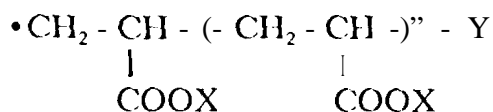
The initiator-derived radicals then react with acrylate monomers to produce the initial propagating radicals for polymerization:



in which $\text{X} = \text{C}_n\text{H}_{2n+1}$, $\text{Y} = \bullet\text{SO}_4^-$, $\bullet\text{SO}_3^-$. Depending on the degree of polymerization and the mode of addition of monomer, the propagating radicals could take the following forms:



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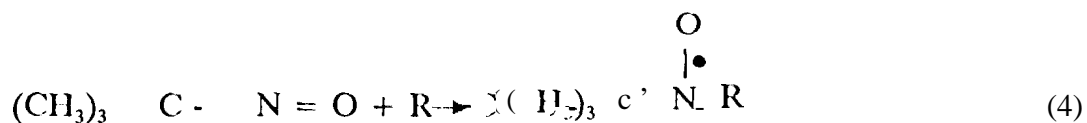


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The presence of end groups, Y, was studied by Ghosh et al¹⁶ in the aqueous redox polymerization of MMA by a dye partition technique. They found that on the average 1.7-2.0 such end groups per polymer chain. In general, the secondary radicals, 1 and 3, are more stable than the primary radicals, 2 and 4.

The EPR spectra of the spin adducts from our experiments are shown in Fig. 1. For both spin traps, two set of experiments were carried out; one, for reaction with the initiator solution only to trap possible initial radicals such as $\bullet SO_4^-$, $\bullet SO_3^-$, or $\bullet OH$, and used as a control, and the second for the reaction with propagating radicals when the spin trap is mixed with the polymerizing BA latex. The latexes treated with spin trap were sampled at different times (10 samples) and studied to see any changes in hyperfine coupling or mobility of the adduct due to continuing polymerization. However, all samples of the same spin trap showed similar EPR spectra without any detectable change.

MNP With this spin trap, the radicals are captured by the following reaction;



in which $R = \bullet SO_4^-$, $\bullet SO_3^-$, $\bullet OH$, or structures 1, 2, 3, 4. Measured hyperfine coupling

constants for nitrogen, a_N and β -hydrogen, $a_{\beta H}$, of the observed spin adducts are listed in Table I. The measured values are in good agreement with the literature values^{12,13,17,18} listed in Table 11, and thus the assignments were made as shown in Table 1.

The angular dependence of β -hydrogen coupling constant, $a_{\beta H}$, can be expressed by the Heller-McConnell equation:^{19,20}

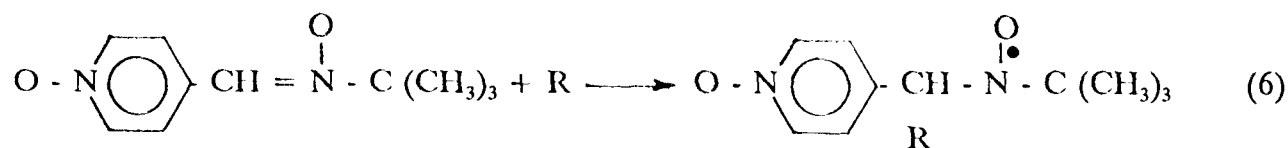
$$a_{\beta H} = (B_1 + B_2 \cos^2 \theta_{11}) \rho_N \quad (5)$$

in which $B_1 = 0$, $B_2 = 50$, $\rho_N = 0.37$ and θ_{11} is the dihedral angle between the plane containing the C-N p-orbital and the plane of N-C β -hydrogen. The value of θ_{11} reflects the differences in the stereoelectronic characteristics of the adducts, and is listed in Table I for comparison.

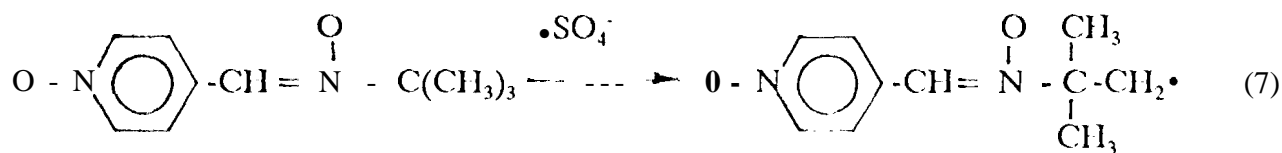
It seems there was no hydroxyl radical detectable from the acidic initiator solution. The samples of MNP + 13A latex show a composite EPR spectrum, consisting of the overlap of a narrow linewidth spectrum observed from the initiator solution with a broader spectrum from the BA oligomer-polymer adducts, 1 and 3. The other radicals, 2 and 4, were not observed, as indicated by the absence of triplet hyperfine splitting from two β -hydrogens of the CH_2 group.^{18,21} This is in agreement with results of other acrylates reported in the literature.^{12,13} The broadening of the spectrum of the spin adduct observed from the BA latex could be due to a combination of unresolved hyperfine interactions with hydrogen atoms in the BA propagating radical and also the slower motion of the nitroxide due to increased molecular weight of the adducts. When we compared the samples collected at different sampling times, e.g., the first and the last one, there was no detectable change in the spectral lineshape. It seems the polymerization process essentially ended when the MNP solution was introduced to the emulsion mixture; the spin trap acted as an effective terminator.

PyOBN The EPR spectra of spin adducts of nitrones show triplets of doublets with a relatively small variations of the doublet splittings, $a_{\beta H}$, as a function of structure of the

trapped radicals.¹¹ In this case, the γ -hydrogen is from the nitron molecule and not from the adducts as shown below:



Compared with the nitroso compounds, the nitrones are more indirect in the identification of radicals, since usually there is no additional hyperfine structure due to the trapped radical. With the nitron spin adducts, small changes in the steric or electronic character of the trapped radical R give rise to detectable variations in the value of $a_{\beta\text{H}}$, which can be utilized to provide information about the chemical structure of the trapped radicals. In Table 111, the measured hyperfine coupling constants from these experiments are compared with the literature values²²⁻²⁸ to aid the assignment. The spin adducts from the initiator solution show hyperfine coupling constants which are similar to the ones listed in the literature²² for the trapped radicals of $\bullet\text{SO}_4^-$. However, when it was scanned with lower modulation amplitude (0.1 G), the spectrum showed extra triplet splittings in each of the doublets as shown in Fig. 1. Expanded spectra of the triplets are shown in Fig. 2. The splitting of 0.32 G is typical of γ -hydrogen splittings observed in the trapping of $\bullet\text{OH}$ radicals by PyOBN (See Table 111). It is speculated²⁹ that the $\bullet\text{SO}_4^-$ radicals in acidic conditions (pH -2) react with the PyOBN by hydrogen abstraction to create radical S:

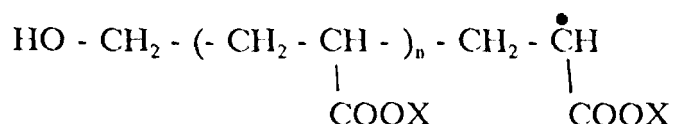


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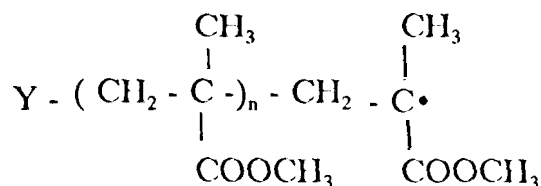
Spin adducts formed by subsequent trapping of radical 5 by another PyOBN molecule will show triplet splittings due to two γ -hydrogens present in the radical.

The spin adducts from BA latex show a rather large value for $a_{\beta H}$, 3.44 G, which corresponds to $\theta_H = 64.45^\circ$. The smaller value of θ_H , thus the large $a_{\beta H}$ is possibly due to the bulky oligomer-polymer BA chain. In the PyOBN case also, the 10 samples of different sampling times showed no detectable change. The EPR spectra showed an overlap of broad background signal, probably due to the spin adducts of high molecular weight oligomer-polymers, 3.

The propagating radicals of acrylates, including 13A, were detected by EPR without the aid of spin-trapping agents by Harris et al³⁰ in their polymerization experiment with ferric chloride-photosensitized UV irradiation reactions in alcohol glasses at low temperatures, -180 - -160°C. However, it should be noted that their conditions are far from those used in normal polymerizations. From their EPR study, they concluded that one type of propagating radical was formed in their experiments for the acrylates studied, namely;



In the emulsion polymerization of MMA, Ballard et al^{3,4} detected radicals and Westmoreland et al^{5,8} reported a nine-line EPR spectrum which has been assigned to the PMMA propagating radical, 6.



6

At temperatures below the glass transition temperature, T_g , of PMMA, the radical had a relatively long life time, however at temperatures near T_g , the radical decayed rapidly by a second-order process⁵. In the case of PBA, the established T_g is 219°K, much lower than

that of PMMA (378°K).³¹ At the peak emulsion polymerization temperature of 60~90°C, the solution is above T_g , and by extrapolation from the PMMA case, one can expect the life time. of the PBA propagating radical to be short ($\ll 1$ sec.). In addition to the differences in T_g , the PBA propagating radical is a secondary radical which is intrinsically less stable than the tertiary radical of the PMMA.

An attempt was made to use PMMA beads (0.1 -0.2 mm dia.) as seeds after swelling with BA. The idea was to capture the short lived BA radicals in a higher T_g PMMA matrices. However, when the reaction mixture of PMMA beads/13A emulsion was sampled in a teflon-polyethylene pipette and quickly frozen in liquid N_2 , the frozen samples did not show any radicals. One of the reasons could be due to the failure in making a homogeneous suspension of the beads, because precipitation and coagulation of the PMMA beads and separation from the reaction mixture were often observed. It seems that the size of the PMMA beads used in the experiments was too large to be used as seeds ($< 500nm$) in the emulsion suspension.³⁻⁶

ACKNOWLEDGEMENT

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Table I. Summary of measured hyperfine coupling constants for nitrogen, a_N , p-hydrogen, $a_{\beta H}$, y-hydrogen, $a_{\gamma H}$, and g values.

Sample	a_N	$a_{\beta H}$	$a_{\gamma H}$	g	assignment
MN] + Initiator	14.69 G	-		2.0056	$\bullet SO_4, \bullet SO_3^-$
MNP + BA Latex	14.08 G	2.65 (i		2.0061	1,3
PyOBN+ Initiator	14.62 G	1.53 G	0.32 G	2.0059	5
PyOBN + BA Latex	15.52 G	3.44 (i		2.0057	1,3

Table 11. Spin Adducts of MNP: Comparison of hyperfine coupling constants for nitrogen, a_N , β -hydrogen, $a_{\beta H}$, γ -hydrogen, $a_{\gamma H}$, and dihedral angle, θ_H .

Radical Adducts	a_N	$a_{\beta H}$	$a_{\gamma H}$	θ_H	Comments
$\bullet SO_4$, $\bullet SO_3^-$	14.68	G -			Madden et al (1991) Ref. 17
	14.69	G -			This work
$\bullet O_2$	26.43 G	0.23 G			Madden et al (1991) Ref. 17
Methyl Acrylate 1, X = CH_3	13.9 G	2.4 G		68.9°	Sato and Otsu (1977) Ref. 12
1,3	14.4 G	2.7 G			Saha et al (1992) Ref. 13
Ethyl Acrylate 1, X = C_2H_5	13.8 G	2.5 G		68.4°	Sato & Otsu (1977) Ref. 12
Butyl Acrylate 1,3 X = C_4H_9	14.08 G	2.65 G		67.8°	This Work
Methyl Methacrylate	14.9 G				Sato & Otsu (1977) Ref. 12
Alkyl Radicals					
$c13Cl I_2\bullet$	15.65 G	10.44 G	0.30 G		Rosenthal et al (1982) Ref. 18
$CH_3CH_2CH_2\bullet$	15.30 G	10.30 G	0.53 G		
$CH_3\dot{C}l$ 1011	14.53 G	2.28 G	-		
$CH_3CH_2\dot{C}HOH$	14.25 G	2.00 G	-		

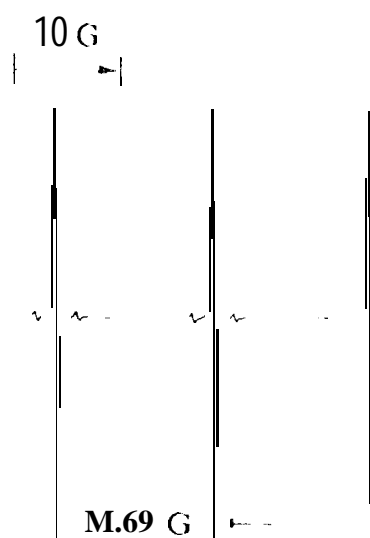
Table III. Spin Adducts of PyOBN: Comparison of hyperfine coupling constants for nitrogen, a_N , and β -hydrogen, $a_{\beta H}$, γ -hydrogen, $a_{\gamma H}$, and dihedral angle, $\theta_{||}$.

Spin Adducts	a_N	$a_{\beta H}$	$a_{\gamma H}$	$\theta_{ }$	Comments
$\bullet SO_4$ ($Na_2S_2O_8$)	14.16 G	1.56 G			pH = 2 - 6 Janzen et al (1978) Ref. 22
	14.96 G	1.41 G			pH = 7,8 Janzen et al (1978) Ref. 22
5	14.62 G	1.53 G	0.32 G		This Work pH = 2
$\bullet OH$ (WO_3 in H_2O)	14.9 G	1.6 G	0.3 G		Leaustic et al (1986) Ref. 23
($Na_2S_2O_8$)	14.97 G	1.68 G	0.36 G		Janzen et al (1978) Ref. 22 and 23
	15.03 G	1.67 G	0.36 G	72.52°	
	15.0 G	1.7 G			Lingford et al (1991) Ref. 25
Butyl Acrylate	15.52 G	3.44 G		64.4s°	This Work
Alkyl Radicals (aqueous solutions)					
$(CH_3)_2\dot{C}OOH$	15.6 G	2.6 G		67.98°	Paraggi et al (1984) Ref. 26
$CH_3\dot{C}HOH$	15.6 G	2.5 G			Lingford et al (1991) Ref. 25
$\bullet ClH_3$	15.91 G	2.75 G			Maillard et al (1979) Ref. 27
$\bullet CH_2CH_2OH$	15.75 G	2.75 G			
$\bullet CH(ClH_3)_2$	15.83 G	2.16 G			
$\bullet C_6H_5$ (phenyl)	15.4 G	3.1 G			Iwahashi et al (1992) Ref. 28
2-chlorophenyl	15.3 G	4.2 G			
2-bromophenyl	15.2 G	4.3 G			

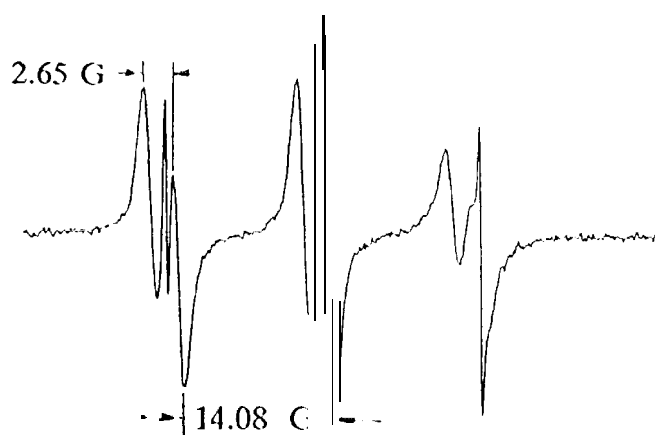
CAPTIONS FOR FIGURES

- Fig. 1. EPR spectra of MNP and PyOBN spin adducts at 20°C.
- Fig. 2. Expanded scan showing details of the triplet splitting of the spin adduct EPR spectrum obtained from PyOBN + initiator solution.

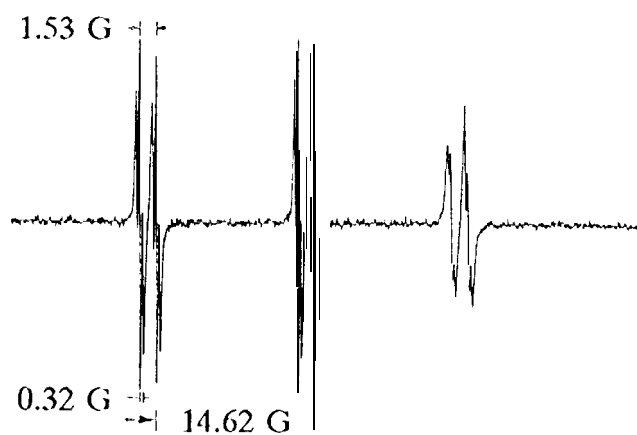
MNP
+ Initiator



MNP
+ BA Latex



PyOBN
+ Initiator



PyOBN
+ BA Latex

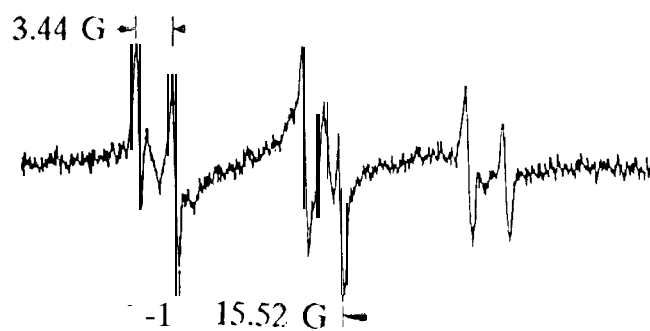


Fig. 1

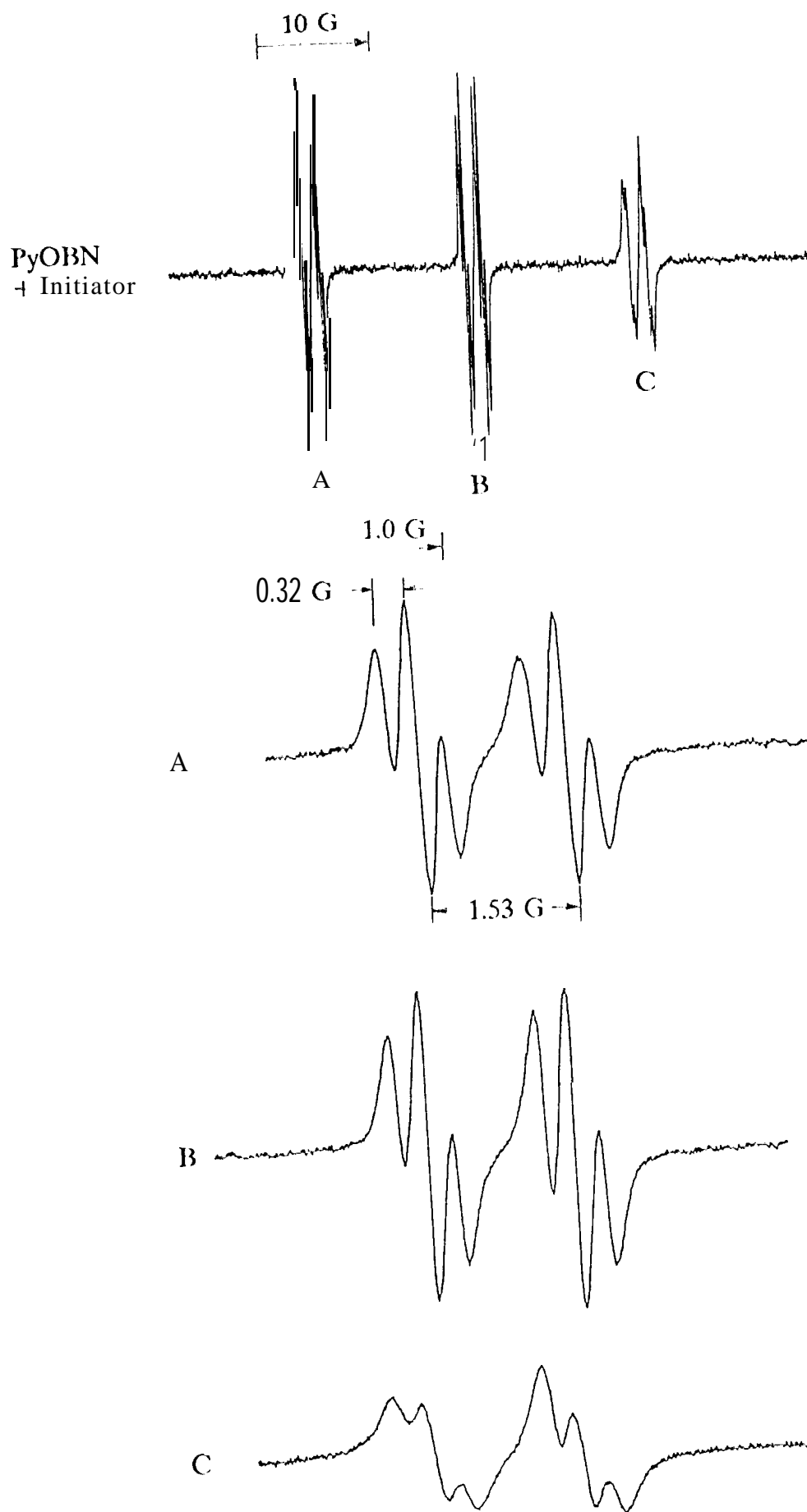


Fig. 2